

<b>REPORT DOCUMENTATION PAGE</b>				<i>Form Approved</i> <i>OMB No. 0704-0188</i>	
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<b>1. REPORT DATE (DD-MM-YYYY)</b> 26-01-2012		<b>2. REPORT TYPE</b> Final Report		<b>3. DATES COVERED (From - To)</b> 9/30/09-9/29/10	
<b>4. TITLE AND SUBTITLE</b> Carbon Nanotube Spaceframes for Low-Density Aerospace Materials				<b>5a. CONTRACT NUMBER</b> FA9550-10-1-0557	
				<b>5b. GRANT NUMBER</b>	
				<b>5c. PROGRAM ELEMENT NUMBER</b>	
<b>6. AUTHOR(S)</b> Nolan Nicholas				<b>5d. PROJECT NUMBER</b>	
				<b>5e. TASK NUMBER</b>	
				<b>5f. WORK UNIT NUMBER</b>	
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> MATRIC				<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>	
<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b> AFOSR/Joycelyn Harrison 875 N Randolph St Arlington, VA 22203				<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b>	
				<b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b> AFRL-OSR-VA-TR-2012-0806	
<b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b> Distribution A					
<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b> <p>The objective of this research effort was to develop and explore chemical processing and analysis techniques for enabling self-assembly of CNTs into controlled architectures. Work focused both on (1) developing chemistries useful for enabling the synthesis of CNT-based objects suitable to enabling self-assembly and on exploring conditions for driving the self-assembly process. A new technique was developed for assaying the surface functional chemistry of chemically treated CNTs was developed to enable high precision quantitative analysis of linkage sites on the CNT surface. Various sidewall functionalization techniques were explored for tailoring the CNT properties. Anomalous behavior was observed for the solubilization properties of amine containing functional groups – these observations will require further exploration to understand the origin and technological implications of these effects. Self-assembly of the targeted nano-architecture was not observed under the conditions explored in this study and provides insights into probable constraints governing this type of self-assembly.</p>					
<b>15. SUBJECT TERMS</b> CNT, solubilization					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>	<b>18. NUMBER OF PAGES</b> 11	<b>19a. NAME OF RESPONSIBLE PERSON</b> Joycelyn Harrison
a. REPORT	b. ABSTRACT	c. THIS PAGE			<b>19b. TELEPHONE NUMBER (Include area code)</b> 703-696-6225

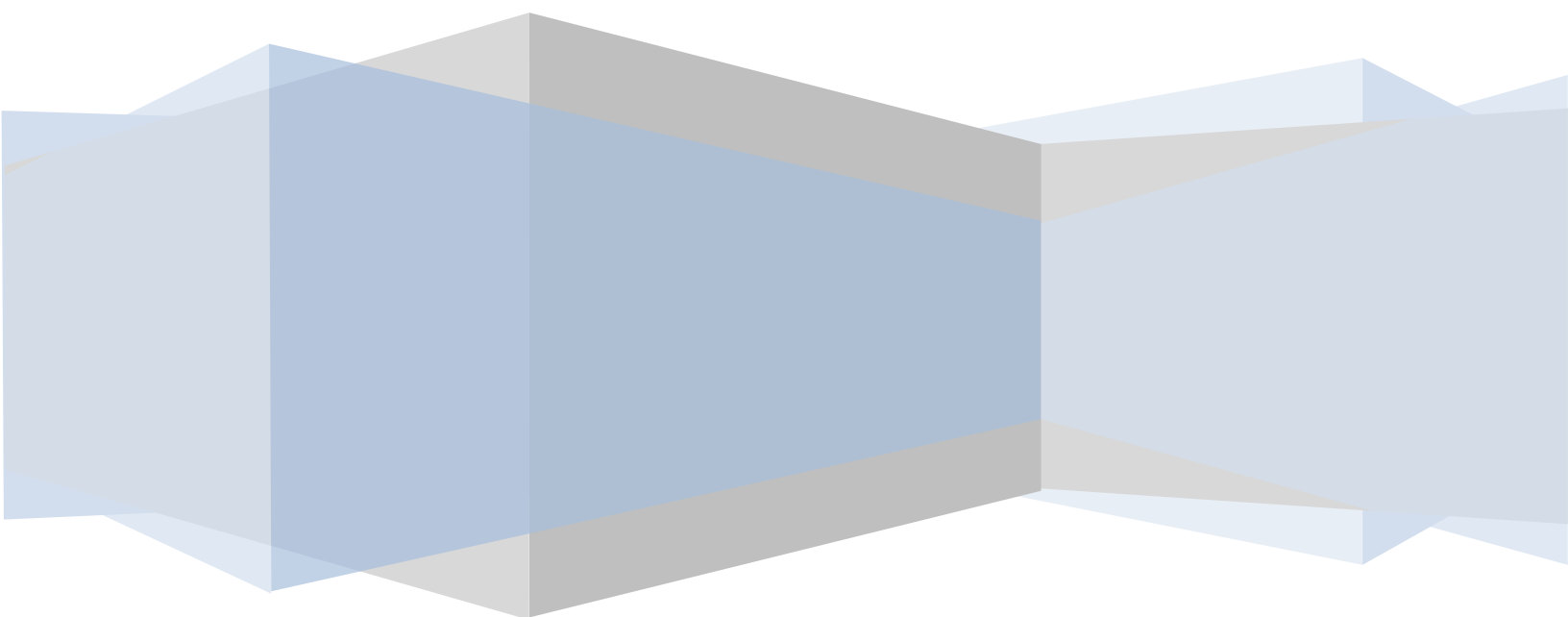
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# **Award FA9550-10-1-0557**

**FINAL REPORT – Carbon Nanotube Spaceframes  
for Low-Density Aerospace Materials**

**Nolan Nicholas**



## Abstract:

The objective of this research effort was to develop and explore chemical processing and analysis techniques for enabling self-assembly of CNTs into controlled architectures. Work focused both on (1) developing chemistries useful for enabling the synthesis of CNT-based objects suitable to enabling self-assembly and on exploring conditions for driving the self-assembly process. A new technique was developed for assaying the surface functional chemistry of chemically treated CNTs was developed to enable high precision quantitative analysis of linkage sites on the CNT surface. Various sidewall functionalization techniques were explored for tailoring the CNT properties. Anomalous behavior was observed for the solubilization properties of amine containing functional groups – these observations will require further exploration to understand the origin and technological implications of these effects. Self-assembly of the targeted nano-architecture was not observed under the conditions explored in this study and provides insights into probable constraints governing this type of self-assembly.

## Background

Computational models predict that nano-architectures composed of carbon nanotubes linked end-to-end to form extended three-dimensional networks will possess advanced materials properties such as high mechanical strength and stiffness per density. An idealized version of such a structure is illustrated in Figure 1. Thus methods to construct such architectures (termed “spaceframes”) represent a highly desirable goal for creating next-generation high performance materials.

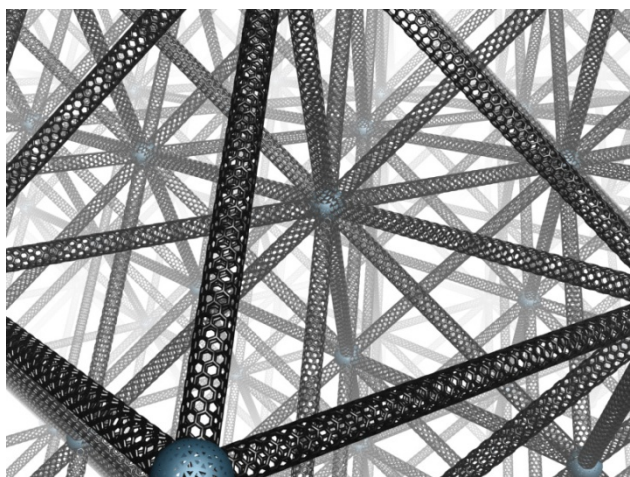


Figure 1: Illustration of the spaceframe concept - provided courtesy of Lockheed Martin Corporation

## Primary Project Objectives

Effective fabrication of CNT materials into spaceframe architectures will require:

- 1) chemical techniques to synthesize tailored nanomaterials with characteristics needed to guide spaceframe self-assembly;

- 2) self-assembly conditions which are effective in assembling chemically sculpted nano-objects into spaceframe architectures.

This project focused on two areas relevant to synthesis of spaceframe architectures.

### Functionalization Methods

Chemically sculpting carbon nanotubes into nano-objects of the type needed for synthesizing CNT spaceframe materials require two distinct functionalization chemistries that produce distinct functional structures at the ends of the nanotubes and on the sidewalls of the nanotubes. These two requirements in turn necessitate that methods are needed to quantifiably assay the outcome of chemical functionalization procedures which are applied to the nanotubes.

In this project, oxidative etching techniques were explored for end selective functionalization. Selective attack on defective sites – which are found in greater density at CNT ends – has been reported in the literature to effect CNT tip opening. Despite this, efficient conditions for achieving tip opening of multi-walled nanotubes without damaging sidewalls have not been generally determined. Many different types of oxidative etching chemistries have been reported in the literature, with acidic conditions such as nitric acid etching and piranha conditions being most commonly utilized. In this project, “RCA” etching under alkaline pH was utilized to allow for more selective etching conditions and reduce the production of adhered fulvic acid species.<sup>1</sup>

A range of RCA type different etching conditions were investigated involving different hydrogen peroxide, ammonium hydroxide and temperature profiles. While methods such as FTIR provide direct evidence that the RCA etch introduces oxygen bearing moieties onto the CNT surface,<sup>2</sup> such methods do not provide simple means to quantify the number of groups produced by the etching process. Additionally, quantitative characterization methods reported in the literature, e.g. titration of acid groups, proved to be cumbersome and highly sensitive to environmental factors.

To resolve these issues in quantitative characterization, we developed a novel assay method for quantifying the number of linkage groups available on the surface of the CNTs. This method is more robust than previous titration based methods and directly reports only available linkage groups without introducing ambiguity over the stereochemistry, differing acid strengths and linkage availability of the CNT surface moieties.

In this method, a dye molecule with strong optical absorbance with well-defined spectral features is provided in excess and reactively linked to the target CNT surface moiety via a reversible reaction (e.g. esterification). Remaining dye is thoroughly removed by rinsing and filtration – leaving only the linkage bound dye present on the CNT surface. The linkage group is then cleaved to yield a quantitative amount the original dye in a free state corresponding to the number of linkage sites which were available on the nanotubes. This process is illustrated in Figure 2.

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<sup>1</sup> Z. Wang, et al.; Carbon (2009); 47, 73-79

<sup>2</sup> T.-C. Hung, et al.; Thin Solid Films (2008); 516, 5236-5240

L. Stobinski, et al.; J. Alloys & Compounds (2010); 501, 77-84

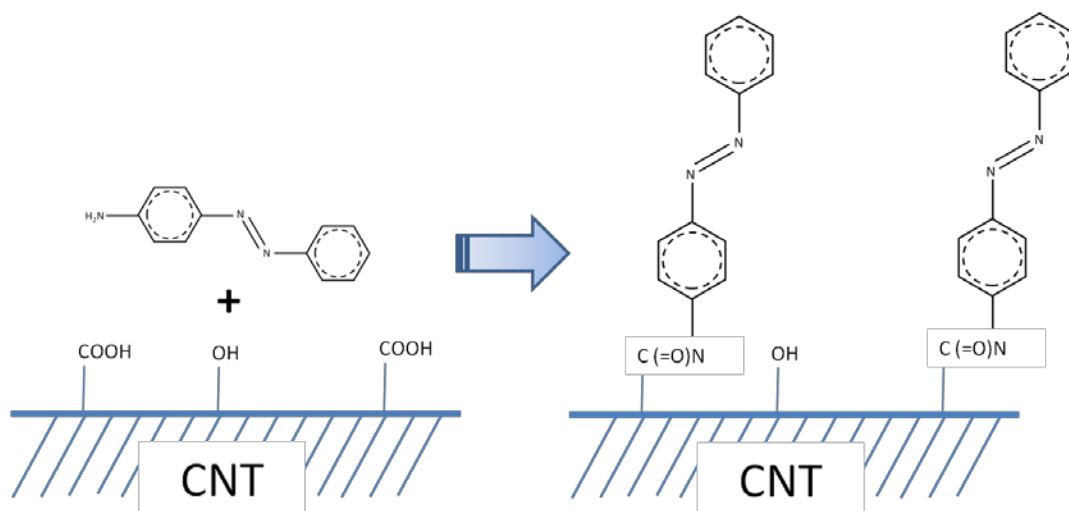


Figure 2: Azo-dye assay linkage

Azo dyes are convenient species for this assay as the conjugated azo bond provides strong optical absorption but is stable against typical conditions needed for condensation and solvolysis type reactions to bind and cleave the dye from the nanotube surface. Aminoazotoluene is an effective assay dye to characterize carboxylic acid sites which are most commonly used for CNT chemistry. This molecule readily undergoes amidation linkage to the CNT surface which can later be cleaved via acid hydrolysis. Similar tests using phenylazophenol yielded less conclusive results, possibly due to the fragility of phenolic esters. Both carboxyl and hydroxyl sites can be simultaneously characterized and utilized for linkage via the aminoazotoluene method by first converting the hydroxyl sites to carboxyl sites via reagents such as succinic anhydride or isocyanatoformates.

This assay has proven remarkably effective and sensitive at quantifying CNT linkage site concentrations and is estimated to be capable of numerically quantifying the presence of linkage sites down to a sensitivity threshold down of approximately  $10^{-8}$  Moles linkage sites per gram of nanotubes. This threshold is theoretically sufficient to quantify the presence of linkage groups at the ends of otherwise pristine nanotubes. This assay provides unprecedented capabilities for characterizing the number of sites specifically available for functionalization present on the CNT surface and when combined with other methods reported in the literature<sup>3</sup> can be utilized to ascertain the efficiency of etching methods for selectively etching the tips of the carbon nanotubes while leaving the sidewalls undamaged.

A broad spectrum of sidewall functionalization techniques which are reported in the literature were explored for applicability to the objectives of this project:

- Carbon radical grafting & moiety transformation
  - benzoyl peroxide free radical grafting followed by sulfonation
  - carbene grafting followed by S<sub>N</sub>2 amination
- Amine linking reactions

<sup>3</sup> L. Jiang & L. Gao; Carbon (2003); 41, 2923–2929

S. Curran, et al.; J. Chem. Phys. (2004); 120, 4886 (5pp)

- Prato azomethine ylide 1,3 dipolar cycloaddition
- oxidative amine radical grafting (amino-PEG)

None of these reactions were found to be suitable conferring effective water solubility.

Carbon radical chemistries were facile in creating efficient linkage of groups to surfaces, but proved ineffective at providing water solubilization. Phenyl sulfonate provides significant water solubility; however, the conditions required for sulfonation are typically highly aggressive and incompatible with the necessity to preserve the chemical identity of opened end groups. Carbene reactions on the other hand, can be made to proceed more selectively; however, the carbon dihalide species bound to the surface are highly water insoluble and proved unreactive toward amino  $S_N2$  chemistries intended to convert these sites to water soluble moieties.

Chemistries which introduced amine functionalities were observed to provide only limited water solubilization. Prato chemistry was utilized to produce pyrrolidine-type amine functionalities on the CNT surface. These materials possessed some limited water solubility not to a sufficient degree to enable the aim of this project. Oxidative linkage was also utilized to graft amino-PEG molecules (surfonamine) to the CNT surface. Characterization indicated successful linkage of these species to the CNTs; however, water solubility was again observed to be below desirable levels. In both cases, functionalized CNT solubility was tested at both at lower pH and after quaternization with methyl iodide with the expectation that amine salt formation would increase the solubility of the product. However, in all cases the solubility was unexpectedly found to be significantly lower upon formation of the salt for reasons which remain to be completely understood.

Other chemistries have been identified to enable the ultimate aims of this project but will remain to be explored in future work.

### Self-Assembly Process

Multiple strategies were tested for tip-to-tip self-assembly of nanotube networks. Though many strategies offer potential for enabling spaceframe-type self-assembly; in this project strategies based upon readily available polymeric species were explored to focus on a systematic exploration of self-assembly conditions with a small variable set.

Polyacid & polybasic polymers were utilized to mediate self-assembly and aggregation of solvated suspensions of carbon nanotubes. Hyperbranched polyethyleneimine (PEI) polymers provide quasi-spherical nano-objects with a significant number of basic amine groups of primary, secondary and tertiary types. These amino groups will associate strongly with acidic sites on etched carbon nanotubes<sup>4</sup> and somewhat less strongly with the pristine sidewall itself.<sup>5</sup> The clustered amine moieties present in PEI will preferentially bind to CNT sites with high local concentrations of acid groups – e.g. CNT ends which have been oxidatively opened.

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<sup>4</sup> M. Marshall, et al.; Carbon (2006); 44, 11-37-1141

<sup>5</sup> D. Chattopadhyay, et al.; J. Am. Chem. Soc. (2003); 125, 3370–3375

Both high ( $M_w = 750$  kDa) and low ( $M_w = 25$  kDa) molecular weight hyperbranched PEI molecules were explored for driving self-assembly. High molecular weight PEI (HW-PEI) is suitably sized to function as a “premade node” – with several opened CNT ends attached to a single globularly shaped PEI molecule. In contrast, low molecular weight PEI (LW-PEI) molecules are too small to act as a node bridging multiple CNTs. Rather, LW-PEI possesses approximately 580 amine groups per molecule which is roughly an order of magnitude more basic amine sites than acid sites typically expected to be present at the end of an etched multi-walled CNT (~15 nm in diameter) and can serve to functionally ‘convert’ the opened ends of the CNTs from acidic to amino-basic sites. Self-assembly of these converted CNT-ends can then be driven by polyacidic species such as poly(vinyl ether-alt-maleic anhydride). Such acid driven self-assembly has advantages over direct poly-amine driven end-to-end assembly primarily in that the acidic sites do not strongly associate with the CNT sidewalls and will not thereby drive sidewall-to-sidewall aggregation in the same way that amine based sites have the potential to do.

Theoretical analysis suggests that CNT self-assembly driven by association with a polyvalent molecular node species which selectively bind with the CNT ends will depend upon the relative concentration of the oxidized CNT end sites versus the concentration of polyvalent node molecules in solution (under ideal conditions the oxidized CNT sites will occur only at opened CNT ends). If the concentration of oxidized CNT sites is much higher than the concentration of polyvalent associative molecules then the CNT aggregation is expected to form small isolated clusters of CNTs assembled around individual nodes while a fraction of the CNTs remain free in suspension. If the concentration of polyvalent associative molecule is much higher than the concentration of oxidized CNT sites then polyvalent species will bind to individual sites without causing self-assembling association. However, when these two concentrations are well-matched then efficient self-assembly of large groups of nanotubes can be achieved. Conditions were found for which both HW-PEI and LW-PEI solutions effectively drive efficient precipitation of CNTs from solution.

Node driven aggregation and self-assembly of CNTs by polyvalent associative molecules was tested for dispersions of oxidized CNTs in organic solvents. HW-PEI driven self-assembly was tested by in a systematic study of self-assembly characteristics versus HW-PEI concentration (at constant CNT concentration) for HW-PEI concentrations spanning two orders of magnitude. Self-assembly driven by polyvalent acid molecules acting on LW-PEI associated on oxidized CNTs were tested in DMF utilizing a constant relative concentration of PEI/CNT and varying the concentration of the polyacid species.

Addition of HW-PEI to dispersions of carbon nanotubes dispersed in organic solvents such as dimethylformamide (DMF) and *n*-methylpyrrolidone (NMP) are observed to drive coalescence of CNTs out of the suspension phase. The efficiency of this process shows a strong dependence upon the relative concentration of HW-PEI versus CNTs in suspension akin to theoretical predictions as illustrated in Figures 3-4. However, imaging of these structures via electron microscopy did not indicate significant tip-to-tip type self-assembly as illustrated in Figure 5. Dicyclohexylcarbodiimide was also added to induce amidation of oxidized CNT acid sites to the PEI amines; however, this addition caused negligible observable difference in the self-assembly process or product.

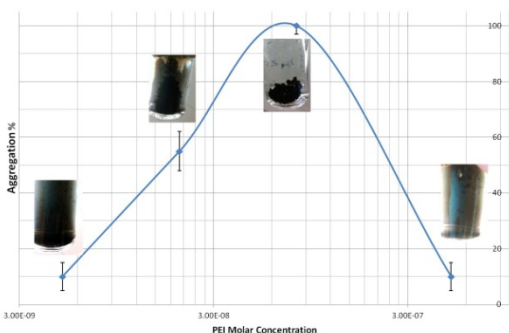


Figure 3: Coalescence v. PEI concentration for CNTs in DMF

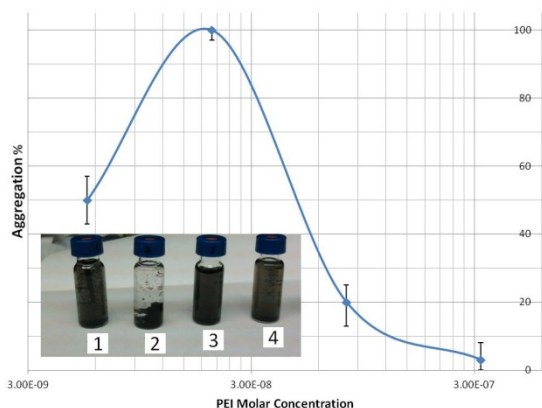


Figure 4: Coalescence v. PEI concentration for CNTs in NMP

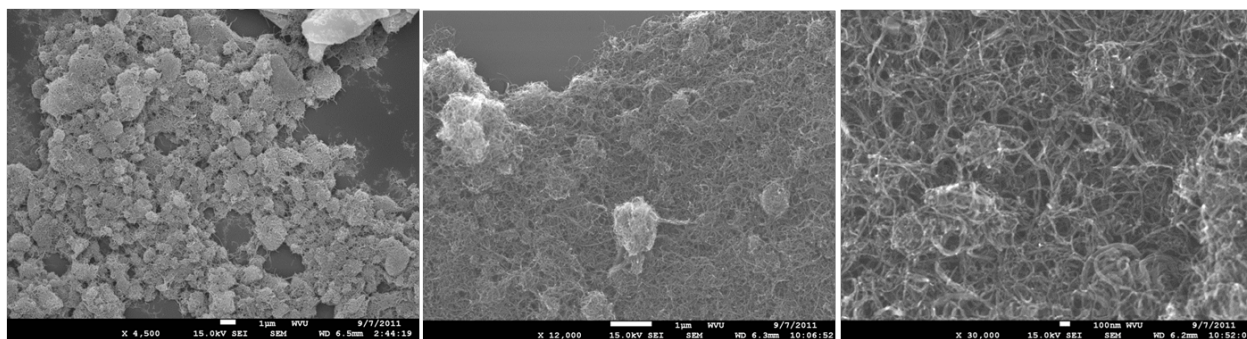


Figure 5: SEM images of CNT coalescence products from HW-PEI systems

For acid association conditions, LW-PEI was added to an organic suspension of oxidized CNTs in DMF to convert clusters of acidic sites into basic sites by linking to the acid sites and possessing an excess of base sites at the linkage. Varied amounts of poly(methyl vinyl ether-alt-maleic anhydride) [ $M_w=216$  kDa] were added into the CNT suspension. High concentrations were observed to lead to no flocculation over relatively long time periods (days) whereas lower concentrations of the polyacid lead to



flocculation within minutes. SEM images of these structures clearly illustrated that they possessed a more open, less dense assembly structure (visually similar to a cloudlike appearance) than those observed for HW-PEI assembly tests as illustrated in Figure 6. However, the structures underwent considerable charging and heating during imaging and which prevented SEM imaging from obtaining high resolution images of their intrinsic structures. Though this charging and heating may itself suggest self-assemblies of the type sought in this work it is not conclusive and will require further exploration to ascertain the morphology of these systems.

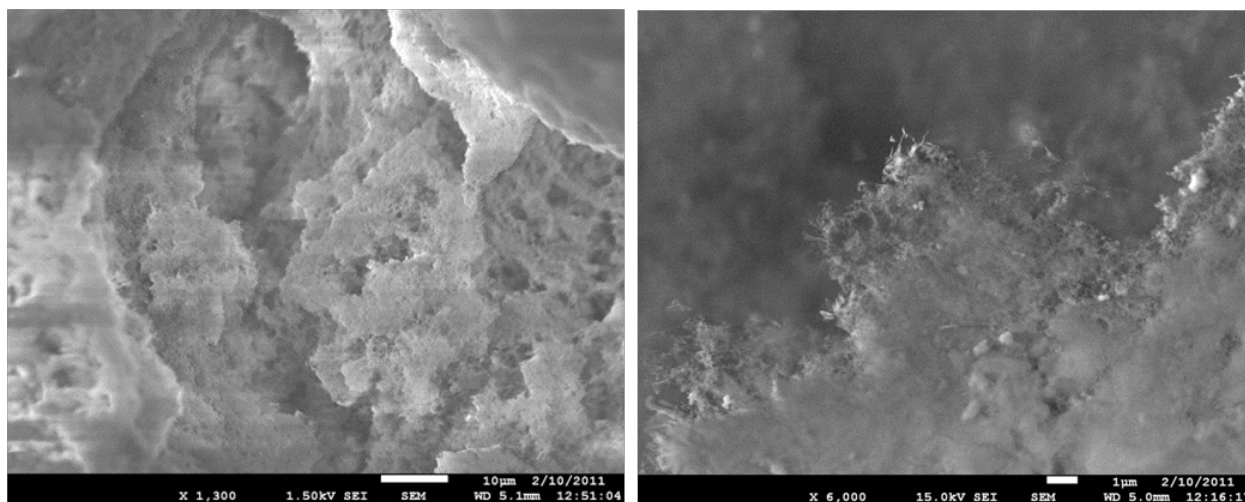


Figure 6: SEM images of CNT coalescence products from LW-PEI / polyacid systems

### Conclusions & Future Work

The results observed for self-assembly tests indicate a greater degree of participation of the CNT sidewalls during the self-assembly process than is desirable. This may indicate either that the PEI possesses stronger than expected affinity for the graphenic basal plane of the CNT sidewall structure or that oxidation was less localized to the tips than desired and was distributed over the CNT sidewalls to a significant degree. Both in-situ tests with DCC during self-assembly and the results of the newly developed dye assay (which was developed partway through this study) are consistent with the hypothesis that the CNTs are “overoxidized” and that a more selective oxidation process is needed to refine the self-assembly procedure. Furthermore, AFM and SEM observations indicate that the CNTs possess a significant degree of deviation from an ‘idealized’ linear morphology and possess considerable intrinsic curvature – often curving back upon themselves. This type of deviation from idealized linearity will create an excluded volume during self-assembly processes which will interfere with tip-to-tip self-assembly in favor of sidewall-to-sidewall collisions and coalescence. This work could not confirm its original planned hypothesis of tip-to-tip assembly of CNTs but rather identified several specific factors which prevented this self-assembly and which can in principle be resolved.

Future explorations of this concept will focus on resolving these factors to produce tip-to-tip CNT architectures. This will start with a refinement of selective etching techniques to ensure that oxidation

occurs selectively at the ends of the carbon nanotubes while leaving the CNT sidewalls intact and free of acidic moieties. The linkage site dye assay will be a key component in refining such a selective etching process. Once this technique has been refined, the use of straight CNTs will be explored – though almost all multi-walled CNTs commercially available today are grown via CVD methods and are not straight it is possible to obtain higher quality, straight CNTs which will be explored in further phases of this work.

## Experimental Methods

### Linkage Site Assay – Dye Amidation

Quantitative assay of functional sites available for linkage chemistry on the surface of carbon nanotubes can be achieved by the use of linkage and subsequent debinding of the dye which enables photometric quantification. This method offers advantage over currently utilized methods by providing increased sensitivity versus current methods such as acid/base titration and greater selectivity of the measurement in measuring only sites available for linkage without interference from unavailable sites.

To quantify a given type of linkage site a dye molecule is chosen which will bind to that particular site. For instance, carboxylic acid sites – which are commonly used in current nanotube linkage chemistry – can be measured by utilizing an amine terminated dye. Applying coupling conditions (addition of a carbodiimide) couple the carboxylate and an excess of amine dye links dye molecules through an amide bond. Excess dye can then be rinsed away, followed by amide bond cleavage and measurement of the amount of dye released.

An example protocol of such an assay is provided below:

- Oxidized carbon nanotubes, excess dye, and excess coupling reagent are added to anhydrous solvent
  - 0.025g oxidized carbon nanotubes (Fenton oxidation conditions)
  - 0.04g o-Aminoazotoluene (97%)
  - 0.075g dicyclohexylcarbodiimide
  - 5ml dry anisole
- Mixture is sonicated briefly to produce a coarse dispersion and allowed to react overnight
- A set of species which react with the coupling agent are added to consume excess
  - 1 ml Lactic Acid solution (80% in water)
- Product is collected by filtration (supported PTFE ~ 450 nm pore size) and rinsed with large excess of isopropanol to remove excess dye and DCU (the byproduct of the coupling reaction)
- Product is dried under vacuum
- A known quantity of the dried product is added to a known quantity of methanol
  - 0.19 g CNT to 3 ml MeOH
  - No coloration is observed to develop after 10 hours of aging – indicating strong binding of the dye molecules to the carbon nanotubes

- A small quantity of concentrated acid is added to hydrolyze amide linkage and debind dye from the carbon nanotubes
  - 100  $\mu$ l concentrated hydrochloric acid (37%)
  - Some solvent coloration is observable within minutes of the addition of acid; sample is allowed to age for 72 hours to ensure full debinding of the dye
- An aliquot of the solvent is then added to a known quantity of pH buffered methanol
  - 300  $\mu$ l aliquot added to 3.5 ml of 0.1N KOAc in MeOH
- Dye concentration is measured by UV-Vis spectroscopy

This same protocol can be applied to measure both carboxylic and hydroxyl type sites together by first using a dicarboxylic acid (preferably in a highly reactive form such as oxalic chloride or succinic anhydride) to first “convert” hydroxyl sites to carboxyl sites.

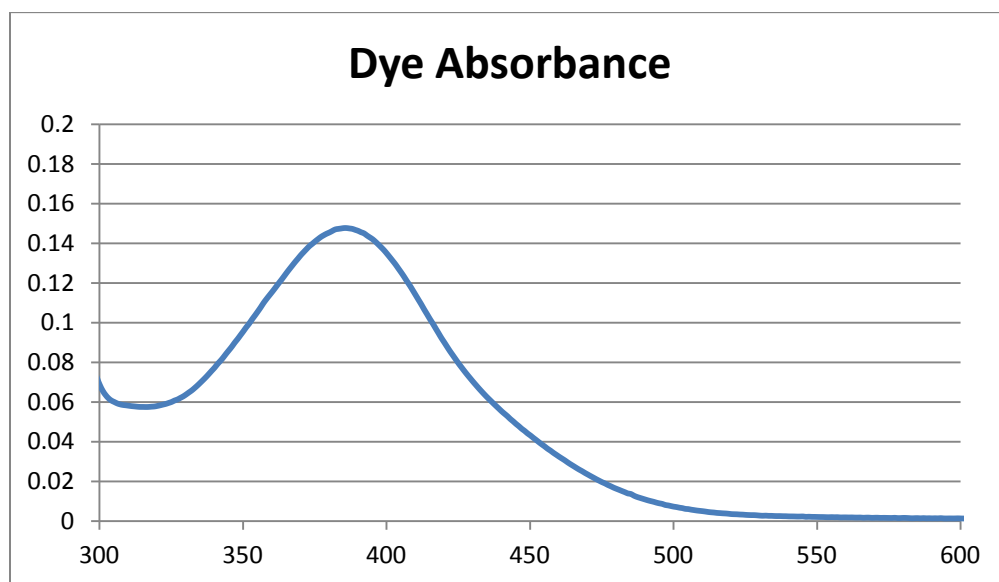


Figure 7: Dye sample absorbance curve from aminoazotoluene assay

Calculated input sample concentration is  $6.83\text{E-}5$  Molar (from a 3ml sample)

- $=2.049\text{E-}7$  Moles Dye
- $=1.09\text{E-}5$  Moles Dye / gram CNT
- $\sim 1.15\text{E-}3$  linkage sites per CNT sidewall atoms (comparison presumes that chemistry is predominated by the outer sidewall & does not get inside the CNT – also presumes CNT morphology)
- At the dye sensitivities available to common instrumentation and through judicious choice of CNT/solvent processing parameters – a sensitivity threshold down to  $\sim 1\text{E-}8$  Mole site / g CNT is estimated to be possible via this process – this is sensitive enough to detect functionalization levels which occur at the ends of otherwise pristine nanotubes.

#### PEI-CNT Self-Assembly Method

Coalescence of oxidized CNTs in organic solvents was accomplished by the addition of controlled amounts of CNTs. The coalescence depends upon the relative concentrations of oxidized sites on the CNTs in solution versus the concentration and size of the PEI molecules. All reagents were used as received without further purification. A typical protocol for such an experiment is as follows:

- Carbon nanotubes (BayTubes) were oxidatively etched under “RCA” etch conditions ( $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$ ) following the report of Datsyuk, et al.<sup>6</sup>
  - The duration, temperature and concentration of the reaction was varied in seeking to achieve end-selective etching conditions
  - CNTs were acidified at the end of the reaction via addition of HCl, then collected via filtration through a PTFE membrane and dried under vacuum
- Oxidized CNTs were dispersed into an organic solvent
  - Oxidized CNTs were sonicated in a bath sonicator in organic solvent (DMF, NMP)
  - Resulting dispersion was gently centrifuged (1 krpm for 5 min) and allowed to settle overnight to remove major agglomerates
  - Resulting dispersion was divided into several small vials
- PEI addition series
  - PEI solution was made to known concentration in 2-propanol and small aliquots of PEI solution were added in known portions to the vials to test flocculation behavior
  - Upon addition of PEI vial was gently vortexed to ensure mixing of the PEI and then placed on the bench for coalescence.
- SEM Preparation & Imaging
  - Samples of the resulting solvent and coalesced structures were drop coated onto silicon substrates and dried (either in air or via supercritical drying)
  - Dried samples were coated in a thin layer (~2nm) platinum via sputter coating
  - Dried and coated samples were imaged via SEM (JEOL JSM-7600F)

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<sup>6</sup> V. Datsyuk, et al.; Carbon (2008); 46, 833 –840